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# PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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[ ] Additional inventors are being named on the \_\_\_\_\_  
 separately numbered sheet(s) attached hereto.

Title of the Invention: FUEL CELL ELECTROCATALYST OF Pt-Ti-W  
 \_\_\_\_\_  
 \_\_\_\_\_

Correspondence Address: Customer Number 000321

ENCLOSED APPLICATION PARTS:

- [X] Specification - Number of Pages 39
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METHOD OF PAYMENT OF FILING FEE:

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Respectfully submitted,



Steven M. Ritchey, Reg. No. 46,321

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FEE TRANSMITTAL

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**FUEL CELL ELECTROCATALYST OF Pt-Ti-W****BACKGROUND OF THE INVENTION****Field of The Invention**

The present invention relates to electrocatalysts, especially to electrocatalysts  
5 which comprise platinum, titanium, and tungsten, which are useful in fuel cell  
electrodes and other electrocatalytic structures.

**Background Information**

A fuel cell is an electrochemical device for directly converting the chemical  
energy generated from an oxidation-reduction reaction of a fuel such as hydrogen or  
10 hydrocarbon-based fuels and an oxidizer such as oxygen gas (in air) supplied  
thereto into a low-voltage direct current. Thus, fuel cells chemically combine the  
molecules of a fuel and an oxidizer without burning, dispensing with the  
inefficiencies and pollution of traditional combustion.

A fuel cell is generally comprised of a fuel electrode (anode), an oxidizer  
15 electrode (cathode), an electrolyte interposed between the electrodes (alkaline or  
acidic), and means for separately supplying a stream of fuel and a stream of oxidizer  
to the anode and the cathode, respectively. In operation, fuel supplied to the anode  
is oxidized, releasing electrons which are conducted via an external circuit to the  
cathode. At the cathode, the supplied electrons are consumed when the oxidizer is  
20 reduced. The current flowing through the external circuit can be made to do useful  
work.

There are several types of fuel cells, including those having electrolytes of:  
phosphoric acid, molten carbonate, solid oxide, potassium hydroxide, and proton  
exchange membrane. A phosphoric acid fuel cell operates at about 160-220 °C,  
25 and preferably at about 190-200 °C. This type of fuel cell is currently being used for  
multi-megawatt utility power generation and for co-generation systems (i.e.,  
combined heat and power generation) in the 50 to several hundred kilowatts range.

In contrast, proton exchange membrane fuel cells use a solid proton-  
conducting polymer membrane as the electrolyte. Typically, the polymer membrane  
30 is maintained in a hydrated form during operation in order to prevent loss of ionic

conduction which limits the operation temperature typically to between about 70 and about 120 °C depending on the operating pressure, and preferably below about 100 °C. Proton exchange membrane fuel cells have a much higher power density than liquid electrolyte fuel cells (e.g., phosphoric acid), and can vary output quickly to meet shifts in power demand. Thus, they are suited for applications such as in automobiles and small scale residential power generation where quick startup is a consideration.

In some applications (e.g., automotive) pure hydrogen gas is the optimum fuel; however, in other applications where a lower operational cost is desirable, a reformed hydrogen-containing gas is an appropriate fuel. A reformed-hydrogen containing gas is produced, for example, by steam-reforming methanol and water at 200-300 °C to a hydrogen-rich fuel gas containing carbon dioxide. Theoretically, the reformat gas consists of 75 vol% hydrogen and 25 vol% carbon dioxide. In practice, however, this gas also contains nitrogen, oxygen, and, depending on the degree of purity, varying amounts of carbon monoxide (up to 1 vol%). Although some electronic devices also reform liquid fuel to hydrogen, in some applications the conversion of a liquid fuel directly into electricity is desirable, as then a high storage density and system simplicity are combined. In particular, methanol is an especially desirable fuel because it has a high energy density, a low cost, and is produced from renewable resources.

For the oxidation and reduction reactions in a fuel cell to proceed at useful rates, especially at operating temperatures below about 300 °C, electrocatalyst materials are typically provided at the electrodes. Initially, fuel cells used electrocatalysts made of a single metal, usually platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), osmium (Os), silver (Ag) or gold (Au) because they are able to withstand the corrosive environment - platinum being the most efficient and stable single-metal electrocatalyst for fuel cells operating below about 300 °C. While these elements were first used in fuel cells in metallic powder form, later techniques were developed to disperse these metals over the surface of electrically conductive supports (e.g., carbon black) to increase the surface area of the electrocatalyst which in turn increased the number of reactive sites leading to improved efficiency of the cell. Nevertheless, fuel cell performance typically declines over time because

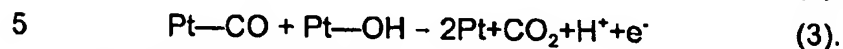
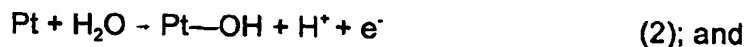
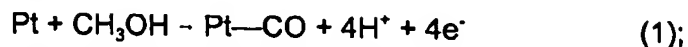


the presence of electrolyte, high temperatures and molecular oxygen dissolve the electrocatalyst and/or sinter the dispersed electrocatalyst by surface migration or dissolution/re-precipitation.

Although platinum is the most efficient and stable single-metal electrocatalyst for fuel cells, it is costly and an increase in electrocatalyst activity over platinum is necessary for wide scale commercialization of fuel cell technology. The development of cathode fuel cell electrocatalyst materials faces longstanding challenges. The greatest challenge is the improvement of the electrode kinetics of the oxygen reduction reaction. In fact, sluggish electrochemical reaction kinetics have prevented attaining the thermodynamic reversible electrode potential for oxygen reduction. This is reflected in exchange current densities of around  $10^{-10}$  to  $10^{-12}$  A/cm<sup>2</sup> for oxygen reduction on, for example, Pt at low and medium temperatures. A factor contributing to this phenomenon includes the fact that the desired reduction of oxygen to water is a four-electron transfer reaction and typically involves breaking a strong O-O bond early in the reaction. In addition, the open circuit voltage is lowered from the thermodynamic potential for oxygen reduction due to the formation of peroxide and possible platinum oxides which inhibit the reaction. A second challenge is the stability of the oxygen electrode (cathode) during long-term operation. Specifically, a fuel cell cathode operates in a regime in which even the most unreactive metals are not completely stable. Thus, alloy compositions which contain non-noble metal elements may have a rate of corrosion which would negatively impact the projected lifetime of a fuel cell. The corrosion may be more severe when the cell is operating near open circuit conditions (which is the most desirable potential for thermodynamic efficiency).

Electrocatalyst materials at the anode also face challenges during fuel cell operation. Specifically, as the concentration of carbon monoxide (CO) rises above about 10 ppm in the fuel the surface of the electrocatalyst can be rapidly poisoned. As a result, platinum (by itself) is a poor electrocatalyst if the fuel stream contains carbon monoxide (e.g., reformed-hydrogen gas typically exceeds 100 ppm). Liquid hydrocarbon-based fuels (e.g., methanol) present an even greater poisoning problem. Specifically, the surface of the platinum becomes blocked with the adsorbed intermediate, carbon monoxide (CO). It has been reported that H<sub>2</sub>O plays

a key role in the removal of such poisoning species in accordance with the following reactions:



As indicated by the foregoing reactions, the methanol is adsorbed and partially oxidized by platinum on the surface of the electrode (1). Adsorbed OH, from the hydrolysis of water, reacts with the adsorbed CO to produce carbon dioxide and a proton (2,3). However, platinum does not form OH species well at the potentials fuel cell electrodes operate (e.g., 200 mV-1.5 V). As a result, step (3) is the slowest step in the sequence, limiting the rate of CO removal, thereby allowing poisoning of the electrocatalyst to occur. This applies in particular to a proton exchange membrane fuel cell which is especially sensitive to CO poisoning because of its low operating temperatures.

One technique for increasing electrocatalytic cathodic activity during the reduction of oxygen and electrocatalytic anodic activity during the oxidation of hydrogen is to employ an electrocatalyst which is more active, corrosion resistant, and/or more poison tolerant. For example, increased tolerance to CO has been reported by alloying platinum and ruthenium at a 50:50 atomic ratio (see, D. Chu and S. Gillman, J. Electrochem. Soc. 1996, 143, 1685). The electrocatalysts proposed to date, however, leave room for further improvement.

#### BRIEF SUMMARY OF THE INVENTION

Briefly, therefore, the present invention is directed to a catalyst for use in oxidation or reduction reactions, the catalyst comprising platinum at a concentration that is no more than 60 atomic percent, titanium, and tungsten.

The present invention is also directed to a catalyst for use in oxidation or reduction reactions, the catalyst comprising platinum, titanium at a concentration of at least 20 atomic percent, and tungsten.

Additionally, the present invention is directed to a catalyst for use in oxidation or reduction reactions, the catalyst comprising platinum, titanium, and tungsten, wherein the concentration of tungsten is at least 25 atomic percent.

The present invention is also directed to a supported electrocatalyst powder for use in electrochemical reactor devices, the supported electrocatalyst powder comprising one of the foregoing catalysts and electrically conductive support particles upon which the catalyst is dispersed.

5 Further, the present invention is directed to a supported electrocatalyst comprising an electrically conductive support and an alloy on the electrically conductive support wherein the alloy comprises one of the foregoing catalysts.

10 The present invention is also directed to a fuel cell electrode, the fuel cell electrode comprising electrocatalyst particles and an electrode substrate upon which the electrocatalyst particles are deposited, the electrocatalyst particles comprising one of the foregoing catalysts.

15 The present invention is also directed to a fuel cell comprising an anode, a cathode, a proton exchange membrane between the anode and the cathode, and one of the foregoing catalysts for the catalytic oxidation of a hydrogen-containing fuel or the catalytic reduction of oxygen.

20 The present invention is also directed to a method for the electrochemical conversion of a hydrogen-containing fuel and oxygen to reaction products and electricity in a fuel cell comprising an anode, a cathode, a proton exchange membrane therebetween, one of the foregoing catalysts, and an electrically conductive external circuit connecting the anode and cathode, the method comprising contacting the hydrogen-containing fuel or the oxygen and the catalyst to catalytically oxidize the hydrogen-containing fuel or catalytically reduce the oxygen.

25 The present invention is also directed to an unsupported catalyst layer on a surface of an electrolyte membrane or an electrode, said unsupported catalyst layer comprising platinum at a concentration that is no more than 60 atomic percent, titanium, and tungsten.

The foregoing and other features and advantages of the present invention will become more apparent from the following description and accompanying drawing.

#### BRIEF DESCRIPTION OF THE DRAWINGS

30 FIG. 1 is a schematic structural view showing essential members of a fuel cell.

FIG. 2 is a side view of a fuel cell.

FIG. 3 is a photograph of an electrode array comprising thin-film alloy compositions deposited on individually addressable electrodes.

#### DETAILED DESCRIPTION OF THE INVENTION

5       The present invention is directed to a metal-containing substance having electrocatalytic activity for use in, for example, fuel cells (e.g., an electrocatalyst). In one embodiment the metal-containing substance is an alloy of the components. However, it is to be noted that the substance (e.g., electrocatalyst) may be a mixture of discrete amounts of the components (e.g., a mixture of metal powders or a  
10       mixture of deposits), wherein a discrete amount of the components may comprise a single component or a combination of components (e.g., an alloy).

      In general, it is desirable to decrease the concentration of noble metals (especially platinum) to reduce the cost of an electrocatalyst. However, as the concentrations of noble metals are decreased, the electrocatalyst may become more  
15       susceptible to corrosion, and/or the activity may be diminished. Thus, it is desirable to achieve the most activity per weight percent of noble metals without compromising, for example, the life cycle of the fuel cell in which the electrocatalyst is placed (see, end current density / weight fraction of platinum as set forth in Table A, *infra*). Additionally, the composition of the present invention is preferably  
20       optimized to limit noble metal concentration while improving corrosion resistance and/or activity, as compared to platinum.

      The present invention is thus directed to a metal-containing substance (e.g., catalyst or alloy) that comprises platinum, titanium, and tungsten. In one  
25       embodiment the present invention is directed to a catalyst consisting essentially of platinum, titanium, and tungsten. Furthermore, the catalyst of the present invention comprises amounts of platinum, titanium, and tungsten which are sufficient for the metals, present therein, to play a role in the catalytic activity and/or crystallographic structure of, for example, the alloy. Stated another way, the concentrations of platinum, titanium, and tungsten are such that the presence of the metals would not  
30       be considered an impurity. For example, the concentrations of each of platinum, titanium, and tungsten are at least about 0.1, 0.5, 1, or even 5 atomic percent.

In one embodiment the catalyst of the present invention comprises at least about 5 atomic percent of platinum. In another embodiment the concentration of platinum is at least about 10 atomic percent. In still another embodiment the concentration of platinum is at least about 20 atomic percent. In another  
5 embodiment of the present invention the concentration of platinum is no more than 60 atomic percent of platinum. In yet another embodiment the concentration of platinum is no more than about 50 atomic percent. In still another embodiment the concentration of platinum is no more than about 45 atomic percent. Accordingly, the concentration of platinum may, in some embodiments, be between about 5 atomic  
10 percent and 60 atomic percent, between about 10 and about 50 atomic percent, and between about 20 and about 45 atomic percent.

In one embodiment the catalyst of the present invention comprises at least about 1 atomic percent of titanium. In another embodiment the concentration of titanium is at least about 5 atomic percent. In another embodiment the  
15 concentration of titanium is at least about 10 atomic percent. In yet another embodiment the concentration of titanium is at least 20 atomic percent. In another embodiment of the present invention the concentration of titanium is no more than about 80 atomic percent. In yet another embodiment the concentration of titanium is no more than about 55 atomic percent. In still another embodiment the  
20 concentration of titanium is no more than about 40 atomic percent. Accordingly, the concentration of titanium may, in some embodiments, be between about 1 and about 80 atomic percent, between about 5 and about 55 atomic percent, between about 10 and about 40 atomic percent, between about 1 and about 55 atomic percent, and between about 5 and about 40 atomic percent.

25 In one embodiment the catalyst of the present invention comprises tungsten at a concentration of at least about 10 atomic percent. In another embodiment the concentration of tungsten is at least about 20 atomic percent. In still another embodiment the concentration of tungsten is at least 25 atomic percent. In yet another embodiment the concentration of tungsten is at least about 30 atomic  
30 percent. In another embodiment of the present invention the concentration of tungsten is no more than about 80 atomic percent. In yet another embodiment the concentration of tungsten is no more than about 60 atomic percent. In still another

embodiment the concentration of tungsten is no more than about 55 atomic percent. Accordingly, the concentration of tungsten may, in some embodiments, be between about 10 and about 80 atomic percent, between about 20 and about 60 atomic percent, and between about 30 and about 55 atomic percent.

5 In view of the foregoing, in one embodiment the catalyst comprises a concentration of platinum that is between about 5 and 60 atomic percent, a concentration of titanium that is less than about 80 atomic percent, and a concentration of tungsten that is between about 10 and about 80 atomic percent. In another embodiment the catalyst comprises a concentration of platinum that is  
10 between about 10 and about 50 atomic percent, a concentration of titanium that is between about 1 and about 55 atomic percent, and a concentration of tungsten that is between about 20 and about 60 atomic percent. In another embodiment the catalyst comprises a concentration of platinum that is between about 20 and about 45 atomic percent, a concentration of titanium that is between about 5 and about 40  
15 atomic percent, and a concentration of tungsten that is between about 30 and about 55 atomic percent. In yet another embodiment the concentration of platinum is between about 30 and about 50 atomic percent, the concentration of titanium is less than about 20 atomic percent, and the concentration of tungsten is between about 40 and about 60 atomic percent. In still another embodiment the concentration of  
20 platinum is between about 35 and about 45 atomic percent, the concentration of titanium is between about 5 and about 15 atomic percent, and the concentration of tungsten is between about 45 and about 55 atomic percent. In yet another embodiment the concentration of platinum is between about 20 and about 40 atomic percent, the concentration of titanium is between about 25 and about 45 atomic  
25 percent, and the concentration of tungsten is between about 30 and about 50 atomic percent. In another embodiment the concentration of platinum is between about 25 and about 35 atomic percent, the concentration of titanium is between about 30 and about 40 atomic percent, and the concentration of tungsten is between about 35 and about 45 atomic percent.

30 In this regard it is to be noted that in one embodiment the substance of the present invention consists essentially of the foregoing metals (e.g., impurities that play little if any role in the catalytic activity and/or crystallographic structure of the

catalyst may be present to some degree). However, in other embodiments it is possible that the substance may comprise other constituents as intentional additions. For example, many metal alloys may comprise oxygen and/or carbon, either as an impurity or as a desired alloy constituent. In view of the foregoing, the alloys of the present invention, while maintaining the same relative amounts of the constituents disclosed herein (i.e., platinum, titanium, and tungsten), may comprise less than 100 percent of the disclosed atoms. Thus, in several embodiments of the present invention the total concentration of the disclosed atoms is greater than about 70, 80, 90, 95, or 99 atomic percent of the substance (e.g., electrocatalyst alloy).

The stoichiometric alloy compositions of the present invention refer to overall stoichiometries, or bulk stoichiometries, of a prepared electrocatalyst prior to being subjected to an electrocatalytic reaction. That is, a reported alloy composition is an average stoichiometry over the entire volume of the prepared electrocatalyst composition, and therefore, localized stoichiometric variations may exist. For example, the volume of an electrocatalyst alloy particle comprising the surface and the first few atomic layers inward therefrom may differ from the bulk stoichiometry. Likewise, within the bulk of the particle there may be stoichiometric variations. The surface stoichiometry corresponding to a particular bulk stoichiometry is highly dependant upon the method and conditions under which the electrocatalyst alloy is prepared and alloys having the same bulk stoichiometry may have significantly different surface stoichiometries. Without being bound to a particular theory, it is believed the differing surface stoichiometries are due at least in part to differences in the atomic arrangements, chemical phases and homogeneity of the electrocatalysts. Further, it has been reported that subjecting an electrocatalyst composition to an electrocatalytic reaction (e.g., the operation of a fuel cell) may change the composition by leaching one or more alloy constituents from the alloy (see, Catalysis for Low Temperature Fuel Cells Part 1: The Cathode Challenges, T.R. Ralph and M.P. Hogarth, Platinum Metals Rev., 2002, 46, (1), p. 3-14). This leaching effect may, in fact, increase the activity of the electrocatalyst by increasing the surface area and/or by changing the surface composition of the electrocatalyst. In fact, the purposeful leaching of electrocatalyst compositions after synthesis to increase the surface area has been disclosed by Itoh et al. in U.S. Pat. No. 5,876,867. As such,

the alloy compositions of the present invention are intended to include starting bulk stoichiometries, any starting surface stoichiometries resulting therefrom, and modifications of the starting bulk and/or surface stoichiometries that are produced by subjecting the electrocatalyst to an electrocatalytic reaction.

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#### Formation of an Electrocatalyst Alloy

The electrocatalyst alloys of the present invention may be formed by a variety of methods. For example, the appropriate amounts of the constituents may be mixed together and heated to a temperature above the respective melting points to form a molten solution of the metals which is cooled and allowed to solidify.

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Typically, electrocatalysts are used in a powder form to increase the surface area which increases the number of reactive sites and leads to improved efficiency of the cell. Thus, the formed metal alloy may be transformed into a powder after being solidified (e.g., by grinding) or during solidification (e.g., spraying molten alloy and allowing the droplets to solidify). It may, however, be advantageous to evaluate alloys for electrocatalytic activity in a non-powder form (see, Examples 1 and 2, *infra*).

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To further increase surface area and efficiency, an electrocatalyst alloy for use in a fuel cell may be deposited over the surface of electrically conductive supports (e.g., carbon black). One method for loading an electrocatalyst alloy onto supports typically comprises depositing metal precursor compounds onto the supports, and converting the precursor compounds to metallic form and alloying the metals using a heat-treatment in a reducing atmosphere (e.g., an atmosphere comprising an inert gas such as argon). One method for depositing the precursor compounds involves chemical precipitation of precursor compounds onto the supports. The chemical precipitation method is typically accomplished by mixing supports and sources of the precursor compounds (e.g., an aqueous solution comprising one or more inorganic metal salts) at a concentration sufficient to obtain the desired loading of the electrocatalyst on the supports and then precipitation of the precursor compounds is initiated (e.g., by adding an ammonium hydroxide solution). The slurry is then typically filtered from the liquid under vacuum, washed

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with deionized water, and dried to yield a powder that comprises the precursor compounds on the supports.

Another method for depositing the precursor compounds comprises forming a suspension comprising a solution and supports suspended therein, wherein the solution comprises a solvent portion and a solute portion that comprises the constituents of the precursor compound(s) being deposited. The suspension is frozen to deposit (e.g., precipitate) the precursor compound(s) on the particles. The frozen suspension is freeze-dried to remove the solvent portion and leave a freeze-dried powder comprising the supports and the deposits of the precursor compound(s) on the supports.

The temperature reached during the thermal treatment is typically at least as high as the decomposition temperature(s) for the precursor compound(s) and not be so high as to result in degradation of the supports and agglomeration of the supports and/or the electrocatalyst deposits. Typically the temperature is between about 60 °C and about 1100 °C. Inorganic metal-containing compounds typically decompose at temperatures between about 600 and about 1000 °C.

The duration of the heat treatment is typically at least sufficient to substantially convert the precursor compounds to the desired state. In general, the temperature and time are inversely related (i.e., conversion is accomplished in a shorter period of time at higher temperatures and vice versa). At the temperatures typical for converting the inorganic metal-containing compounds to a metal alloy set forth above, the duration of the heat treatment is typically at least about 30 minutes. In one embodiment, the duration is between about 2 and about 12 hours.

#### Unsupported Catalyst or Alloys in Electrode/Fuel Cell Applications

It is to be noted that, in another embodiment of the present invention, the metal substance (e.g., catalyst or alloy) may be unsupported; that is, it may be employed in the absence of a support particle. More specifically, it is to be noted that in another embodiment of the present invention a metal catalyst or alloy, comprising platinum, titanium, and tungsten, may be directly deposited (e.g., sputtered) onto, for example, (i) a surface of one or both of the electrodes (e.g., the anode, the cathode or both), and/or (ii) one or both surfaces of a polyelectrolyte

membrane, and/or (iii) some other surface, such as a backing for the membrane (e.g., carbon paper).

In this regard it is to be further noted that each component (e.g., metal) of the catalyst or alloy may be deposited separately, each for example as a separate layer  
5 on the surface of the electrode, membrane, etc. Alternatively, two or more components may be deposited at the same time. Additionally, in the case of an alloy, the alloy may be formed and then deposited, or the components thereof may be deposited and then the alloy subsequently formed thereon.

Deposition of the component(s) may be achieved using means known in the  
10 art, including for example known sputtering techniques (see, e.g., PCT Application No. WO 99/16137). Generally speaking, however, in one approach sputter-deposition is achieved by creating, within a vacuum chamber in an inert atmosphere, a voltage differential between a target component material and the surface onto which the target component is to be deposited, in order to dislodge particles from the  
15 target component material which are then attached to the surface of, for example, an electrode or electrolyte membrane, thus forming a coating of the target component thereon. In one embodiment, the components are deposited on a polymeric electrolyte membrane, including for example (i) a copolymer membrane of tetrafluoroethylene and perfluoropolyether sulfonic acid (such as the membrane  
20 material sold under the trademark NAFION), (ii) a perfluorinated sulfonic acid polymer (such as the membrane material sold under the trademark ACIPLEX), (iii) polyethylene sulfonic acid polymers, (iv) polyketone sulfonic acids, (v) polybenzimidazole doped with phosphoric acid, (vi) sulfonated polyether sulfones, and (vii) other polyhydrocarbon-based sulfonic acid polymers.

It is to be noted that the specific amount of each metal or component of the  
25 catalyst or alloy may be controlled independently, in order to tailor the composition to a given application. In some embodiments, however, the amount of each deposited component may be less than about 5 mg/cm<sup>2</sup> of surface area (e.g., electrode surface area, membrane surface area, etc.), less than about 1 mg/cm<sup>2</sup>, less than  
30 about 0.5 mg/cm<sup>2</sup>, less than about 0.1 mg/cm<sup>2</sup>, or even less than about 0.05 mg/cm<sup>2</sup>. Alternatively, in some embodiments the amount of the deposited

component, or alloy, may range from about 0.5 mg/cm<sup>2</sup> to less than about 5 mg/cm<sup>2</sup>, or from about 0.1 mg/cm<sup>2</sup> to less than about 1 mg/cm<sup>2</sup>.

It is to be further noted that the specific amount of each component, and/or the conditions under which the component is deposited, may be controlled in order to control the resulting thickness of the component, or alloy, layer on the surface of the electrode, electrolyte membrane, etc. For example, as determined by means known in the art (e.g., scanning electron microscopy or Rutherford back scattering spectrophotometric method), the deposited layer may have a thickness ranging from several angstroms (e.g., about 2, 4, 6, 8, 10 or more) to several tens of angstroms (e.g., about 20, 40, 60, 80, 100 or more), up to several hundred angstroms (e.g., about 200, 300, 400, 500 or more). Additionally, after all of the components have been deposited, and/or alloyed (or, alternatively, after the alloy has been deposited), the layer of the multi-component metal substance of the present invention may have a thickness ranging from several tens of angstroms (e.g., about 20, 40, 60, 80, 100 or more), up to several hundred angstroms (e.g., about 200, 400, 600, 800, 1000, 1500 or more). Thus, in different embodiments the thickness may be, for example, between about 10 and about 500 angstroms, between about 20 and about 200 angstroms, and between about 40 and about 100 angstroms.

It is to be still further noted that in embodiments wherein a catalyst or alloy (or the components thereof) are deposited as a thin film on the surface of, for example, an electrode or electrolyte membrane, the composition of the deposited catalyst or alloy may be as previously described herein. Additionally, in other embodiments, the composition of the deposited catalyst or alloy may be other than as previously described. For example, with respect to an embodiment of an unsupported catalyst or alloy, the concentration of the platinum may be greater than 60 atomic percent.

#### Incorporation of the Electrocatalyst Compositions in a Fuel Cell

Although the alloy compositions of the present invention can be used in any type of fuel cell (e.g., phosphoric acid, molten carbonate, solid oxide, potassium hydroxide, and proton exchange membrane), they are particularly suited for use in proton exchange membrane fuel cells. As shown in FIGS. 1 and 2, a fuel cell, generally indicated **21**, comprises a fuel electrode (anode) **2** and an air electrode,

oxidizer electrode (cathode) 3. In between the electrodes 2 and 3, a proton exchange membrane 1 serves as an electrolyte and it is usually a strongly acidic ion exchange membrane such as a perfluorosulphonic acid-based membrane.

Preferably, the proton exchange membrane 1, the anode 2, and the cathode 3 are integrated into one body to minimize contact resistance between the electrodes and the proton exchange membrane. Current collectors 4 and 5 engage the anode and the cathode, respectively. A fuel chamber 8 and an air chamber 9 contain the respective reactants and are sealed by sealants 6 and 7, respectively.

In general, electricity is generated by hydrogen-containing fuel combustion (i.e., the hydrogen-containing fuel and oxygen react to form water, carbon dioxide and electricity). This is accomplished in the above-described fuel cell by introducing the hydrogen-containing fuel F into the fuel chamber 8, while oxygen O (preferably air) is introduced into the air chamber 9, whereby an electric current can be immediately transferred between the current collectors 4 and 5 through an outer circuit (not shown). Ideally, the hydrogen-containing fuel is oxidized at the anode 2 to produce hydrogen ions, electrons, and possibly carbon dioxide gas. The hydrogen ions migrate through the strongly acidic proton exchange membrane 1 and react with oxygen and electrons transferred through the outer circuit to the cathode 3 to form water. If the hydrogen-containing fuel F is methanol, it is preferably introduced as a dilute acidic solution to enhance the chemical reaction, thereby increasing power output (e.g., a 0.1 M methanol/0.5 M sulfuric acid solution).

To prevent the loss of ionic conduction in the proton exchange membranes, they typically remain hydrated during operation of the fuel cell. As a result, the material of the proton exchange membrane is typically selected to be resistant to dehydration at temperatures up to between about 100 and about 120 °C. Proton exchange membranes usually have reduction and oxidation stability, resistance to acid and hydrolysis, sufficiently low electrical resistivity (e.g.,  $<10 \Omega \cdot \text{cm}$ ), and low hydrogen or oxygen permeation. Additionally, proton exchange membranes are usually hydrophilic. This ensures proton conduction (by reversed diffusion of water to the anode), and prevents the membrane from drying out thereby reducing the electrical conductivity. For the sake of convenience, the layer thickness of the

membranes is typically between 50 and 200  $\mu\text{m}$ . In general, the foregoing properties are achieved with materials which have no aliphatic hydrogen-carbon bonds, which, for example, are achieved by replacing hydrogen with fluorine or by the presence of aromatic structures; the proton conduction results from the incorporation of sulfonic acid groups (high acid strength). Suitable proton-conducting membranes also include perfluorinated sulfonated polymers such as NAFION and its derivatives produced by E.I. du Pont de Nemours & Co., Wilmington, Delaware. NAFION is based on a copolymer made from tetrafluoroethylene and perfluorovinylether, and is provided with sulfonic groups working as ion-exchanging groups. Other suitable proton exchange membranes are produced with monomers such as perfluorinated compounds (e.g., octafluorocyclobutane and perfluorobenzene), or even monomers with C—H bonds which, in a plasma polymer, do not form any aliphatic H atoms which could constitute attack sites for oxidative breakdown.

The electrodes of the present invention comprise the electrocatalyst compositions of the present invention and an electrode substrate upon which the electrocatalyst is deposited. In one embodiment the electrocatalyst alloy is directly deposited on the electrode substrate. In another embodiment the electrocatalyst alloy is supported on electrically conductive supports and the supported electrocatalyst is deposited on the electrode substrate. The electrode may also comprise a proton conductive material that is in contact with the electrocatalyst. The proton conductive material may facilitate contact between the electrolyte and the electrocatalyst, and may thus enhance fuel cell performance. Preferably, the electrode is designed to increase cell efficiency by enhancing contact between the reactant (i.e., fuel or oxygen), the electrolyte and the electrocatalyst. In particular, porous or gas diffusion electrodes are typically used since they allow the fuel/oxidizer to enter the electrode from the face of the electrode exposed to the reactant gas stream (back face), and the electrolyte to penetrate through the face of the electrode exposed to the electrolyte (front face), and reaction products, particularly water, to diffuse out of the electrode.

The electrically conductive support particles typically comprise an inorganic material such as carbon. However, the support particles may comprise an organic

material such as an electrically conductive polymer (see, U.S. Pat. Appl. 2002/0132040 A1). Carbon supports may be predominantly amorphous or graphitic and they may be prepared commercially, or specifically treated to increase their graphitic nature (e.g., heat treated at a high temperature in vacuum or in an inert gas atmosphere) thereby increasing corrosion resistance. For example, it may be oil furnace black, acetylene black, graphite paper, carbon fabric, or carbon aerogel. A carbon aerogel preferably has an electrical conductivity of between  $10^{-2}$  and  $10^3 \Omega^{-1} \cdot \text{cm}^{-1}$  and a density of between 0.06 and 0.7 g/cm<sup>3</sup>; the pore size is between 20 and 100 nm (porosity up to about 95%). Carbon black support particles may have a Brunauer, Emmett and Teller (BET) surface area up to about 2000 m<sup>2</sup>/g. It has been reported that satisfactory results are achieved using carbon black support particles having a high mesoporous area, e.g., greater than about 75 m<sup>2</sup>/g (see, *Catalysis for Low Temperature Fuel Cells Part 1: The Cathode Challenges*, T.R. Ralph and M.P. Hogarth, *Platinum Metals Rev.*, 2002, 46, (1), p. 3-14). Experimental results to date indicate that a surface area of about 500 m<sup>2</sup>/g is preferred.

Preferably, the proton exchange membrane, electrodes, and electrocatalyst materials are in contact with each other. This is typically accomplished by depositing the electrocatalyst either on the electrode, or on the proton exchange membrane, and then placing the electrode and membrane in contact. The alloy electrocatalysts of this invention can be deposited on either the electrode or the membrane by a variety of methods, including plasma deposition, powder application (the powder may also be in the form of a slurry, a paste, or an ink), chemical plating, and sputtering. Plasma deposition generally entails depositing a thin layer (e.g., between 3 and 50  $\mu\text{m}$ , preferably between 5 and 20  $\mu\text{m}$ ) of an electrocatalyst composition on the membrane using low-pressure plasma. By way of example, an organic platinum compound such as trimethylcyclopentadienylplatinum is gaseous between  $10^{-4}$  and 10 mbar and can be excited using radio-frequency, microwaves, or an electron cyclotron resonance transmitter to deposit platinum on the membrane. According to another procedure, electrocatalyst powder is distributed onto the proton exchange membrane surface and integrated at an elevated temperature under pressure. If, however, the amount of electrocatalyst particles exceeds about 2

mg/cm<sup>2</sup> the inclusion of a binder such as polytetrafluoroethylene is common.

Further, the electrocatalyst may be plated onto dispersed small support particles (e.g., the size is typically between 20 and 200 Å, and more preferably between about 20 and 100 Å). This increases the electrocatalyst surface area which in turn

5 increases the number of reaction sites leading to improved cell efficiency. In one such chemical plating process, for example, a powdery carrier material such as conductive carbon black is contacted with an aqueous solution or aqueous suspension (slurry) of compounds of metallic components constituting the alloy to permit adsorption or impregnation of the metallic compounds or their ions on or in  
10 the carrier. Then, while the slurry is stirred at high speed, a dilute solution of suitable fixing agent such as ammonia, hydrazine, formic acid, or formalin is slowly added dropwise to disperse and deposit the metallic components on the carrier as insoluble compounds or partly reduced fine metal particles.

The loading, or surface concentration, of an electrocatalyst on the membrane  
15 or electrode is based in part on the desired power output and cost for a particular fuel cell. In general, power output increases with increasing concentration; however, there is a level beyond which performance is not improved. Likewise, the cost of a fuel cell increases with increasing concentration. Thus, the surface concentration of electrocatalyst is selected to meet the application requirements. For example, a fuel  
20 cell designed to meet the requirements of a demanding application such as an extraterrestrial vehicle will usually have a surface concentration of electrocatalyst sufficient to maximize the fuel cell power output. For less demanding applications, economic considerations dictate that the desired power output be attained with as little electrocatalyst as possible. Typically, the loading of electrocatalyst is between  
25 about 0.01 and about 6 mg/cm<sup>2</sup>. Experimental results to date indicate that in some embodiments the electrocatalyst loading is preferably less than about 1 mg/cm<sup>2</sup>, and more preferably between about 0.1 and 1 mg/cm<sup>2</sup>.

To promote contact between the collector, electrode, electrocatalyst, and  
30 membrane, the layers are usually compressed at high temperature. The housings of the individual fuel cells are configured in such a way that a good gas supply is ensured, and at the same time the product water can be discharged properly.

Typically, several fuel cells are joined to form stacks, so that the total power output is increased to economically feasible levels.

In general, the electrocatalyst compositions and fuel cell electrodes of the present invention may be used to electrocatalyze any fuel containing hydrogen (e.g.,  
5 hydrogen and reformed-hydrogen fuels). Also, hydrocarbon-based fuels may be used including saturated hydrocarbons such as methane (natural gas), ethane, propane and butane; garbage off-gas; oxygenated hydrocarbons such as methanol and ethanol; and fossil fuels such as gasoline and kerosene; and mixtures thereof.

To achieve the full ion-conducting property of proton exchange membranes,  
10 in some embodiments suitable acids (gases or liquids) are typically added to the fuel. For example,  $\text{SO}_2$ ,  $\text{SO}_3$ , sulfuric acid, trifluoromethanesulfonic acid or the fluoride thereof, also strongly acidic carboxylic acids such as trifluoroacetic acid, and volatile phosphoric acid compounds may be used ("Ber. Bunsenges. Phys. Chem.", Volume 98 (1994), pages 631 to 635).

#### Fuel Cell Uses

As set forth above, the alloy compositions of the present invention are useful as electrocatalysts in fuel cells which generate electrical energy to perform useful work. For example, the alloy compositions may be used in fuel cells which are in electrical utility power generation facilities; uninterrupted power supply devices;  
20 extraterrestrial vehicles; transportation equipment such as heavy trucks, automobiles, and motorcycles (see, Fuji et al., U.S. Pat. No. 6,048,633; Shinkai et al., U.S. Pat. No. 6,187,468; Fuji et al., U.S. Pat. No. 6,225,011; and Tanaka et al., U.S. Pat. No. 6,294,280); residential power generation systems; mobile communications equipment such as wireless telephones, pagers, and satellite  
25 phones (see, Prat et al., U.S. Pat. No. 6,127,058 and Kelley et al., U.S. Pat. No. 6,268,077); mobile electronic devices such as laptop computers, personal data assistants, audio recording and/or playback devices, digital cameras, digital video cameras, and electronic game playing devices; military and aerospace equipment such as global positioning satellite devices; and robots.

#### Example 1



Forming Electrocatalytic Alloys on Individually Addressable Electrodes

The electrocatalyst alloy compositions set forth in Table A, *infra*, were prepared using the combinatorial techniques disclosed in Warren et al., U.S. Pat. No. 6,187,164; Wu et al., U.S. Pat. No. 6,045,671; Strasser, P., Gorer, S. and Devenney, M., *Combinatorial Electrochemical Techniques For The Discovery of New Fuel-Cell Cathode Materials*, Nayayanan, S.R., Gottesfeld, S. and Zawodzinski, T., eds., Direct Methanol Fuel Cells, Proceedings of the Electrochemical Society, New Jersey, 2001, p. 191; and Strasser, P., Gorer, S. and Devenney, M., *Combinatorial Electrochemical Strategies For The Discovery of New Fuel-Cell Electrode Materials*, Proceedings of the International Symposium on Fuel Cells for Vehicles, 41st Battery Symposium, The Electrochemical Society of Japan, Nagoya 2000, p. 153. For example, an array of independent electrodes (with areas of between about 1 and 3 mm<sup>2</sup>) may be fabricated on inert substrates (e.g., glass, quartz, sapphire alumina, plastics, and thermally treated silicon). The individual electrodes were located substantially in the center of the substrate, and were connected to contact pads around the periphery of the substrate with wires. The electrodes, associated wires, and contact pads were fabricated from a conducting material (e.g., titanium, gold, silver, platinum, copper or other commonly used electrode materials).

Specifically, the alloy compositions set forth in Table A were prepared using a photolithography/RF magnetron sputtering technique (GHz range) to deposit thin-film alloys on arrays of 64 individually addressable electrodes. A quartz insulating substrate was provided and photolithographic techniques were used to design and fabricate the electrode patterns on it. By applying a predetermined amount of photoresist to the substrate, photolyzing preselected regions of the photoresist, removing those regions that have been photolyzed (e.g., by using an appropriate developer), depositing a layer of titanium about 500 nm thick using RF magnetron sputtering over the entire surface and removing predetermined regions of the deposited titanium (e.g. by dissolving the underlying photoresist), intricate patterns of individually addressable electrodes were fabricated on the substrate.

Referring to FIG. 3, the fabricated array 20 consisted of 64 individually addressable electrodes 21 (about 1.7 mm in diameter) arranged in an 8 x 8 square that were insulated from each other (by adequate spacing) and from the substrate

24 (fabricated on an insulating substrate), and whose interconnects 22 and contact pads 23 were insulated from the electrochemical testing solution (by the hardened photoresist or other suitable insulating material).

After the initial array fabrication and prior to depositing the electrocatalyst alloys for screening, a patterned insulating layer covering the wires and an inner portion of the peripheral contact pads, but leaving the electrodes and the outer portion of the peripheral contact pads exposed (preferably approximately half of the contact pad is covered with this insulating layer) was deposited. Because of the insulating layer, it is possible to connect a lead (e.g., a pogo pin or an alligator clip) to the outer portion of a given contact pad and address its associated electrode while the array is immersed in solution, without having to worry about reactions that can occur on the wires or peripheral contact pads. The insulating layer was a hardened photoresist, but any other suitable material known to be insulating in nature could have been used (e.g., glass silica, alumina, magnesium oxide, silicon nitride, boron nitride, yttrium oxide, or titanium dioxide).

Following the creation of the titanium coated array, a steel mask having 64 holes (1.7 mm in diameter) was pressed onto the substrate to prevent deposition of sputtered material onto the insulating resist layer. The deposition of the electrocatalyst alloys was also accomplished using RF magnetron sputtering and a two shutter masking system as described by Wu et al. which enable the deposition of material onto 1 or more electrodes at a time. Each individual thin-film electrocatalyst alloy is created by a super lattice deposition method. For example, when preparing a ternary alloy electrocatalyst composition, metals M1, M2 and M3 are to be deposited and alloyed onto one electrode. First, a metal M1 sputter target is selected and a thin film of M1 having a defined thickness is deposited on the electrode. This initial thickness is typically from about 3 to about 12 Å. After this, metal M2 is selected as the sputter target and a layer of M2 is deposited onto the layer of M1. The thickness of M2 layer is also from about 3 to about 12 Å. The thicknesses of the deposited layers are in the range of the diffusion length of the metal atoms (e.g., about 10 to about 30 Å) which allows in-situ alloying of the metals. Then, a layer of M3 is deposited onto the M1-M2 alloy forming a M1-M2-M3 alloy film. As a result of the three deposition steps, an alloy thin-film (9 - 25 Å

thickness) of the desired stoichiometry is created. This concludes one deposition cycle. In order to achieve the desired total thickness of a cathode electrocatalyst material, deposition cycles are repeated as necessary which results in the creation of a super lattice structure of a defined total thickness (typically about 700 Å).

Although the number, thickness (stoichiometry) and order of application of the individual metal layers may be determined manually, it is desirable to utilize a computer program to design an output file which contains the information necessary to control the operation of the sputtering device during the preparation of a particular library wafer (i.e., array). One such computer program is the LIBRARY STUDIO software available from Symyx Technologies, Inc. of Santa Clara, California and described in European Patent No. 1080435 B1. The compositions of several as sputtered alloy compositions were analyzed using x-ray fluorescence (XRF) to confirm that they were consistent with desired compositions (chemical compositions determined using x-ray fluorescence are within about 5% of the actual composition).

An array was prepared to evaluate the specific alloy compositions set forth in Table A below. On the array one electrode consisted essentially of platinum and it served as an internal standard for the screening operation.

Table A

Electrode Number	End Current Density (Absolute Activity) mA/cm <sup>2</sup>	End Current Density per Weight Fraction of Pt	Relative Activity Compared to Internal Pt	Pt atomic %	Ti atomic %	W atomic %
34	-4.42	-11.69	29.24	31	21	48
17	-2.59	-10.39	17.15	18	32	50
25	-2.65	-9.28	17.52	22	27	51
10	-2.48	-9.23	16.38	18	39	43
35	-4.07	-9.19	26.90	36	23	42
9	-1.86	-8.75	12.28	15	37	48
33	-2.75	-8.61	18.22	26	21	53
27	-3.40	-8.35	22.48	31	29	40
49	-3.20	-8.31	21.16	35	7	58
41	-2.92	-8.28	19.34	30	14	55
2	-1.86	-8.13	12.28	15	44	41
3	-2.30	-7.94	15.24	18	46	36

	42	-3.06	-7.43	20.22	35	15	50
	28	-3.39	-7.10	22.46	36	30	34
	52	-3.04	-6.73	20.09	40	11	49
5	19	-2.24	-6.05	14.80	26	35	39
	4	-2.11	-5.88	13.96	22	48	30
	12	-2.35	-5.87	15.57	27	42	31
	15	-1.96	-5.76	12.98	15	71	13
	26	-1.90	-5.55	12.59	26	28	46
10	20	-2.42	-5.49	16.00	31	37	32
	18	-1.40	-4.57	9.26	22	34	44
	5	-1.97	-4.50	13.04	27	50	24
	13	-2.05	-4.28	13.58	31	44	24
	45	-2.03	-4.05	13.43	41	22	37
15	6	-2.06	-3.91	13.63	32	52	16
	11	-1.27	-3.84	8.40	22	41	37
	38	-1.73	-3.07	11.41	41	34	25
	7	-1.27	-2.02	8.43	37	55	9
	14	-0.82	-1.43	5.41	36	46	17
20	31	-0.69	-1.07	4.55	41	46	13
	37	-0.33	-0.85	2.19	28	34	38
	46	-0.28	-0.43	1.83	53	22	25
	39	-0.30	-0.41	1.96	54	34	12
	53	-0.20	-0.34	1.33	53	11	36
25	50	-0.04	-0.27	0.29	15	11	74
	43	-0.03	-0.15	0.19	15	23	63
	64	-0.15	-0.15	1.00	100	0	0
	36	-0.01	-0.07	0.10	15	34	51
	21	-0.01	-0.02	0.08	36	38	25
30	29	0.00	-0.01	0.02	15	46	38
	22	0.00	0.00	0.01	15	59	26
	44	0.00	0.00	0.00	28	23	50
	30	0.00	0.00	0.00	28	46	25
	51	0.00	0.01	-0.01	27	11	61
	23	0.01	0.01	-0.04	29	58	13
35	1	0.00	0.02	-0.03	11	42	47

Example 2Screening Alloys for Electrocatalytic Activity

The alloy compositions set forth in Table A that were synthesized on arrays according to the method set forth in Example 1 were screened for electrochemical reduction of molecular oxygen to water to determine relative electrocatalytic activity against the internal and/or external platinum standard.

In general, the array wafers were assembled into an electrochemical screening cell and a screening device established an electrical contact between the 64 electrode electrocatalysts (working electrodes) and a 64-channel multi channel potentiostat used for the screening. Specifically, each wafer array was placed into a screening device such that all 64 spots are facing upward and a tube cell body that was generally annular and having an inner diameter of about 2 inches (5 cm) was pressed onto the upward facing wafer surface. The diameter of this tubular cell was such that the portion of the wafer with the square electrode array formed the base of a cylindrical volume while the contact pads were outside the cylindrical volume. A liquid ionic solution (i.e., 1 M  $\text{HClO}_4$  aqueous electrolyte) was poured into this cylindrical volume and a common counter electrode (i.e., platinum gauze), as well as a common reference electrode (e.g., mercury/mercury sulfate reference electrode (MMS)), were placed into the electrolyte solution to close the electrical circuit.

A rotator shaft with blades was also placed into the electrolyte to provide forced convection-diffusion conditions during the screening. The rotation rate was typically between about 300 to about 400 rpm. Depending on the screening experiment either argon or pure oxygen was bubbled through the electrolyte during the measurements. Argon served to remove  $\text{O}_2$  gas in the electrolyte to simulate  $\text{O}_2$ -free conditions used for the initial conditioning of the electrocatalysts. The introduction of pure oxygen served to saturate the electrolyte with oxygen for the oxygen reduction reaction. During the screening, the electrolyte was maintained at 60 °C and the rotation rate was constant. Three groups of tests were performed to screen the activity of the electrocatalysts. The electrolyte was purged with argon for about 20 minutes prior to the electrochemical measurements. The first group of tests comprised cyclic voltammetric measurements while purging the electrolyte with argon. Specifically, the first group of tests comprised:

- a. a potential sweep from open circuit potential (OCP) to about +0.3 V to about -0.63 V and back to about +0.3 V at a rate of about 20 mV/s;
- b. twelve consecutive potential sweeps from OCP to about +0.3 V to about -0.7 V and back to about +0.3 V at a rate of about 200 mV/s; and

- c. a potential sweep from OCP to about +0.3 V to about -0.63 V and back to about +0.3 V at a rate of about 20 mV/s.

The electrolyte was then purged with oxygen for approximately 30 minutes. The following second group of tests were performed while continuing to purge with

5 oxygen:

- a. measuring the OCP for a minute; then, starting at OCP the voltage was swept down to about -0.4 V at a rate of about 10 mV/s;
- b. measuring the OCP for a minute; then applying a potential step from OCP to about +0.1 V while measuring the current for about 5 minutes;
- 10 and
- c. measuring the OCP for a minute; then applying a potential step from OCP to about +0.2 V while monitoring the current for about 5 minutes.

The third group of tests comprised a repeat of the second group of tests after about one hour from completion of the second group of tests. The electrolyte was

15 continually stirred and purged with oxygen during the waiting period. All the foregoing test voltages are with reference to a mercury/mercury sulfate (MMS) electrode. Additionally, an external platinum standard comprising an array of 64 platinum electrodes in which the oxygen reduction activity of the 64 platinum electrodes averaged -0.35 mA/cm<sup>2</sup> at +0.1V vs. a mercury/mercury sulfate electrode

20 was used to monitor the tests to ensure the accuracy of the oxygen reduction evaluation.

The specific alloy compositions set forth in Table A were prepared and screened in accordance with the above-described methods and the results are set forth therein. The screening results in Table A are for the third test group steady

25 state currents at +0.1 V MMS. The current value reported (End Current Density) is the result of averaging the last three current values of the chronoamperometric test normalized for geometric surface area. Referring to Table A, the alloy compositions corresponding to Electrode Numbers 34, 17, 25, 10, 35, 9, 33, 27, 49, 41, 2, 3, 42, 28, 52, 19, 4, 12, 15, 26, 20, 18, 5, 13, 45, 6, 11, 38, 7, 14, 31, 37, 46, 39, 53, 50,

30 and 43 exhibited an oxygen reduction activity greater than the internal platinum standard.

Example 3Synthesis of Supported Electrocatalyst Alloys

The synthesis of  $\text{Pt}_{30}\text{Ti}_{22}\text{W}_{48}$  alloys (see, Table B, Target Catalyst Comp.,  
infra) on carbon support particles was attempted according to different process  
5 conditions in order to evaluate the performance of the alloys while in a state that is  
typically used in fuel cell. To do so, the alloy component precursors were deposited  
or precipitated on supported platinum powder (i.e., platinum nanoparticles supported  
on carbon black particles). Platinum supported on carbon black is commercially  
available from companies such as Johnson Matthey, Inc., of New Jersey and E-Tek  
10 Div. of De-Nora, N.A., Inc., of Sommerset, New Jersey. Such supported platinum  
powder is available with a wide range of platinum loading. The supported platinum  
powder used in this example had a nominal platinum loading of about 40 or 20  
percent by weight, a platinum surface area of between about 150 and about 170  
 $\text{m}^2/\text{g}$  (determined by CO adsorption), a combined carbon and platinum surface area  
15 between about 350 and about 400  $\text{m}^2/\text{g}$  (determined by  $\text{N}_2$  adsorption), and an  
average particle size of less than about 0.5 mm (determined by sizing screen).

Referring to Table B, the electrocatalyst alloy corresponding to the target  
composition of  $\text{Pt}_{30}\text{Ti}_{22}\text{W}_{48}$  (HFC 181 and 182) was formed on carbon support  
particles using a freeze-drying precipitation method. The freeze-drying method  
20 comprised forming a precursor solution comprising the desired metal atoms in the  
desired concentrations. Each of the supported alloys were prepared in an  
analogous manner with variations in the amounts of metal-containing compounds.  
For example, the target  $\text{Pt}_{30}\text{Ti}_{22}\text{W}_{48}$  alloy composition (HFC 182) was prepared by  
dissolving about 0.042 g of  $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  and about 0.082 g of  
25  $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$  in a vial containing about 5 ml of  $\text{H}_2\text{O}$ . The vial was capped and  
the contents were heated to about 100 °C for 2 minutes until the metal-containing  
compounds were dissolved, yielding a slightly hazy solution. This solution was  
introduced into a HDPE vial containing the 0.200 g of supported platinum powder  
which had a nominal platinum loading of about 19.2 percent by weight resulting in a  
30 black suspension. The suspension was homogenized by immersing a probe of a  
BRANSON SONIFIER 150 into the vial and sonicating the mixture for about 30  
seconds at a power level of 3. Subsequently, the titanium-containing solution was

introduced into the vial, which contained the suspension of the carbon supported platinum and tungsten-containing solution. The suspension was further homogenized by sonicating the mixture for an additional 90 seconds at a power level of 3. The vial containing the homogenized suspension was then immersed in a liquid nitrogen bath for about 3 minutes to solidify the suspension. The solid suspension was then freeze-dried for about 24 hours using a LABONCO FREEZE DRY SYSTEM (Model 79480) to remove the solvent. The tray and the collection coil of the freeze dryer were maintained at about 27 °C and about -48 °C, respectively, while evacuating the system (the pressure was maintained at about 0.15 mbar).

After freeze-drying, the vial contained a powder comprising the supported platinum powder, and the tungsten and titanium precursors deposited thereon.

The recovered precursor powders were then subjected to a heat treatment to reduce the precursors to their metallic state, and to alloy the metals with each other and the platinum on the carbon black particles. One particular heat treatment comprised heating the powder in a quartz flow furnace with an atmosphere comprising about 6% H<sub>2</sub> and 94% Ar using a temperature profile of room temperature to about 40 °C at a rate of about 5 °C/min; holding at about 40 °C for 2 hours; increasing the temperature to about 200 °C at a rate of 5 °C/min; holding at about 200 °C for two hours; increasing the temperature at a rate of about 5 °C/min to about 700 or 900 °C; holding at a max temperature of about 700 or 900 °C for a duration of about two or seven hours (indicated in Table B); and cooling down to room temperature.

In order to determine the actual composition of the supported electrocatalyst alloys, the differently prepared alloys (e.g., by composition variation or by heat treatment variation) were subjected to EDS (Electron Dispersive Spectroscopy) elemental analysis. The sample powders were compressed into 6 mm diameter pellets with a thickness of about 1 mm. The target alloy composition and actual composition for the prepared supported electrocatalyst alloys are also set forth in Table B.



Table B

Powder Name	Target Catalyst Comp.	Max Alloying Temp for a duration (°C / hrs)	Actual Catalyst Comp.	Target Pt Loading (wt%)	Measured Pt Loading (wt%)	Log Pt Mass Activity at +0.15 V MMS	Pt Mass Activity at +0.15 V MMS (mA/mg Pt)	Relative performance at +0.15 V MMS	Catalyst Mass Activity at +0.15 V MMS (mA/mg)
HFC 10	Pt		Pt	37.8	37.8	2.11	128.82	1.00	48.7
HFC 181	Pt <sub>30</sub> Ti <sub>22</sub> W <sub>48</sub>	700 / 7	Pt <sub>30</sub> Ti <sub>24</sub> W <sub>46</sub>	14.4	14.4	2.51	325.76	2.53	46.91
HFC 182	Pt <sub>30</sub> Ti <sub>22</sub> W <sub>48</sub>	900 / 2	---	14.4	---	---	---	---	41.85
HFC 181-2	Pt <sub>30</sub> Ti <sub>22</sub> W <sub>48</sub>	700 / 7	Pt <sub>30</sub> Ti <sub>24</sub> W <sub>46</sub>	14.4	14.4	2.54	346.29	2.69	49.87

Example 4Evaluating the Electrocatalytic Activity of Supported Electrocatalysts

The supported alloy electrocatalysts set forth in Table B and formed according to Example 3 were subjected to electrochemical measurements to evaluate their activities. For the evaluation, the supported alloy electrocatalysts were applied to a rotating disk electrode (RDE) as is commonly used in the art (see, Rotating disk electrode measurements on the CO tolerance of a high-surface area Pt/Vulcan carbon fuel cell electrocatalyst, Schmidt et al., Journal of the Electrochemical Society (1999), 146(4), 1296-1304; and Characterization of high-surface-area electrocatalysts using a rotating disk electrode configuration, Schmidt et al., Journal of the Electrochemical Society (1998), 145(7), 2354-2358). Rotating disk electrodes are a relatively fast and simple screening tool for evaluating supported electrocatalysts with respect to their intrinsic electrolytic activity for oxygen reduction (e.g., the cathodic reaction of a fuel cell).

The rotating disk electrode was prepared by depositing an aqueous-based ink that comprises the support electrocatalyst and a NAFION solution on a glassy carbon disk. The concentration of electrocatalyst powder in the NAFION solution was about 1 mg/mL. The NAFION solution comprised the perfluorinated ion-exchange resin, lower aliphatic alcohols and water, wherein the concentration of resin is about 5 percent by weight. The NAFION solution is commercially available from the ALDRICH catalog as product number 27,470-4. The glassy carbon electrodes were 5 mm in diameter and were polished to a mirror finish. Glassy carbon electrodes are commercially available, for example, from Pine Instrument Company of Grove City, Pennsylvania. An aliquot of 10  $\mu$ L electrocatalyst suspension was added to the carbon substrate and allowed to dry at a temperature between about 60 and 70 °C. The resulting layer of NAFION and electrocatalyst was less than about 0.2  $\mu$ m thick. This method produced slightly different platinum loadings for each electrode made with a particular suspension, but the variation was determined to be less than about 10 percent by weight.

After being dried, the rotating disk electrode was immersed into an electrochemical cell comprising an aqueous 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution maintained at room temperature. Before performing any measurements, the

electrochemical cell was purged of oxygen by bubbling argon through the electrolyte for about 20 minutes. All measurements were taken while rotating the electrode at about 2000 rpm, and the measured current densities were normalized either to the glassy carbon substrate area or to the platinum loading on the electrode. Two groups of tests were performed to screen the activity of the supported electrocatalysts. The first group of tests comprised cyclic voltammetric measurements while purging the electrolyte with argon. Specifically, the first group comprised:

- a. two consecutive potential sweeps starting from OCP to about +0.35V then to about -0.65V and back to OCP at a rate of about 50 mV/s;
- b. two hundred consecutive potential sweeps starting from OCP to about +0.35V then to about -0.65V and back to OCP at a rate of about 200 mV/s; and
- c. two consecutive potential sweeps starting from OCP to about +0.35V then to about -0.65V and back to OCP at a rate of about 50 mV/s.

The second test comprised purging with oxygen for about 15 minutes followed by a potential sweep test for oxygen reduction while continuing to purge the electrolyte with oxygen. Specifically, potential sweeps from about -0.45 V to +0.35 V were performed at a rate of about 5 mV/s to evaluate the initial activity of the electrocatalyst as a function of potential and to create a geometric current density plot. The electrocatalysts were evaluated by comparing the diffusion corrected activity at 0.15 V. All the foregoing test voltages are with reference to a mercury/mercury sulfate electrode. Also, it is to be noted that the oxygen reduction measurements for a glassy carbon RDE without an electrocatalyst did not show any appreciable activity within the potential window.

The above-described supported electrocatalyst alloy compositions were evaluated in accordance with the above-described method and the results are set forth in Table B. The carbon supported alloy target composition of  $\text{Pt}_{30}\text{Ti}_{22}\text{W}_{48}$  for sample HFC 181 exhibited oxygen reduction activities greater than that of carbon supported platinum. The results of the evaluation also indicate, among other things, that it may take numerous iterations to develop a set of parameters for producing the

target alloy composition. Also evidenced by the data, is that activity can be adjusted by changes in the processing conditions.

Further, without being held to a particular theory, it is presently believed that differences in activity for similar alloy compositions may be due to several factors such as alloy homogeneity (e.g., an alloy, as defined below, may have regions in which the constituent atoms show a presence or lack of order, i.e., regions of solid solution within an ordered lattice, or some such superstructure), changes in the lattice parameter due to changes in the average size of component atoms, changes in particle size, and changes in crystallographic structure/symmetry. The ramifications of structure and symmetry changes are often difficult to predict. For example, in the Pt-Ti system, as the amount of titanium added to platinum increases, the lattice of the resulting alloy may be expected to change from a cubic face centered lattice (100% platinum) to a structurally similar cubic primitive lattice ( $Pt_3Ti$ ). Upon further addition of titanium, the resulting structure may change significantly as compared to the original cubic face centered lattice. Within the Pt-W system, solid solutions have been reported at the composition of PtW, however other structure types unrelated to the cubic face centered lattice have also been described. In the ternary Pt-Ti-W system, some combination of both behaviors may be expected however differences in metal radius or electronic characteristics as well as exact synthetic conditions make it difficult to predict exactly what may occur. Without being held to a particular theory, the possibility exists that as the relative ratio of titanium and tungsten to platinum increases, a solid solution may crystallize (e.g., Ti/W and Pt may mix randomly within some concentration limits, or under some specific synthesis conditions), and out of this solid solution an ordered phase may gradually crystallize (e.g.,  $Pt(Ti,W)$ ) only to return to a solid solution (disordered alloy) and again back to an ordered phase as the formula  $Pt_{30}Ti_{24}W_{46}$  is reached. Symmetry changes (e.g., those associated with the changes from a cubic face centered structure to a primitive cubic structure, for example) may result in significant changes in the x-ray diffraction pattern. These changes may also be accompanied by more subtle changes in lattice parameters that may be indicative of the resulting changes in the size of the respective metal constituents. For example, the 12-coordinate metallic radii of platinum, titanium and tungsten are 1.39 D, 1.47 D, and 1.41 D, respectively, and as

one metal is substituted for another, the average metal radius, and consequently the observed lattice parameter may be expected to shrink or expand accordingly. The average radius may thus be used as an indicator of lattice changes as a function of stoichiometry, or alternatively, as an indicator of stoichiometry based on observed  
5 lattice parameters. It should be noted, however, that while average radii may be useful as a general rule, experimental results should be expected to conform only in a general manner because local ordering, significant size disparity between atoms, significant changes in symmetry, and other factors may produce values that are inconsistent with expectations. Occasionally the use of alternative metallic radii may  
10 be useful. One such alternative radius concept approximates metal radii using known crystallographically ordered Pt-based alloys such as  $\text{Pt}_3\text{Ti}$  or  $\text{Pt}_{50}\text{W}_{50}$  (in both cases, cubic symmetry is maintained) instead of pure metals. In this case, the same close-packed geometric arguments are relevant with the exception that the lattice parameter of the ordered metal alloy is used in conjunction with the accepted  
15 12-coordinate metallic radius of platinum, supra. Using these concepts, effective radii of titanium and tungsten are 1.35 D and 1.395 D, respectively.

An interpretation of XRD analyses for the foregoing supported alloys is set forth below. Interpretation of XRD analyses can be subjective, and therefore, the following conclusions are not intended to be limiting.

20  $\text{Pt}_{30}\text{Ti}_{24}\text{W}_{46}$  (HFC 181 and 182). The predicted change in average radius based on the targeted stoichiometry was an increase of approximately 0.2% versus platinum. XRD measurements of HFC 181 indicated a very slight decrease (-0.1%) compared to platinum, however small levels of non-alloyed titanium and tungsten metals were present. XRD measurements of HFC 182 indicated a slight increase  
25 (+0.6%) compared to platinum. It is noted that impurity levels are difficult to establish, however peak shape irregularities indicate their likely presence. No obvious ordering is seen in either sample.

In view of the foregoing, for a particular electrocatalyst composition a determination of the optimum conditions is preferred to produce the highest activity  
30 for that particular composition. In fact, for certain electrocatalyst compositions, different structural characteristics may define what exactly is described as a "good" electrocatalyst. These characteristics may include differences in the crystallinity,

crystallographic ordering and/or particle size. These characteristics are not necessarily predictable. Additionally, for example, the starting materials used to synthesize the alloy may play a role in the activity of the synthesized alloy.

Specifically, using something other than a metal nitrate salt solution to supply the

metal atoms may result in different activities. Freeze-drying and heat treatment parameters such as atmosphere, time, temperature, etc. may also need to be optimized. This optimization may involve balancing competing phenomena. For

example, increasing the heat treatment temperature is generally known to improve the reduction of a metal salt to a metal which typically increases activity; however, it

also tends to increase the size of the electrocatalyst alloy particle and decrease surface area, which decreases electrocatalytic activity.

#### Definitions

Activity is defined as the maximum sustainable, or steady state, current (Amps) obtained from the electrocatalyst, when fabricated into an electrode, at a given electric potential (Volts). Additionally, because of differences in the geometric area of electrodes, when comparing different electrocatalysts, activity is often expressed in terms of current density (A/cm<sup>2</sup>). An alloy is a mixture comprising two or more metals. An alloy may be described as a solid solution in which the solute and solvent atoms (the term solvent is applied to the metal that is in excess) are arranged at random, much in the same way as a liquid solution may be described. If some solute atoms replace some of those of the solvent in the structure of the latter, the solid solution may be defined as a substitutional solid solution. Alternatively, an interstitial solid solution is formed if a smaller atom occupies the interstices between the larger atoms. Combinations of the two types are also possible. Furthermore, in certain solid solutions, some level of regular arrangement may occur under the appropriate conditions resulting in a partial ordering that may be described as a superstructure. These solid solutions may have characteristics that may be distinguishable through characterization techniques such as XRD. Significant changes in XRD may be apparent due to changes in symmetry, if more complete ordering occurs such as that which occurs between Pt metal and Pt<sub>3</sub>Ti. Although the global arrangement of the atoms is extremely similar in both cases, the relationship

between the locations of the Pt and Ti atoms is now ordered and not random resulting in different diffraction patterns. Further, a homogeneous alloy is a single compound comprising the constituent metals. A heterogeneous alloy comprises an intimate mixture of crystals of individual metals and/or metallic compounds (see, 5 Structural Inorganic Chemistry, A.F. Wells, Oxford University Press, 5th Edition, 1995, chapter 29). An alloy, as defined herein, is also meant to include materials which may comprise elements which are generally considered to be non-metallic. For example, some alloys of the present invention may comprise oxygen in atomic, molecular, and/or metallic oxide form. Additionally, some alloys of the present 10 invention may comprise carbon in atomic, molecular, and/or metal carbide form. If present, the amount of oxygen and/or carbon in the alloy is typically at what is generally considered to be a low level (e.g., less than about 5 weight percent), however higher concentrations are also possible (e.g., up to about 10 weight percent).

15 It is to be understood that the above description is intended to be illustrative and not restrictive. Many embodiments will be apparent to those of skill in the art upon reading the above description. The scope of the invention should therefore be determined not with reference to the above description alone, but should be determined with reference to the claims and the full scope of equivalents to which 20 such claims are entitled.

**CLAIMS**

What is claimed is:

1. A catalyst for use in oxidation or reduction reactions, the catalyst comprising platinum at a concentration that is no greater than 60 atomic percent, titanium, and tungsten.
2. The catalyst of claim 1 wherein the concentration of platinum is no greater than about 50 atomic percent.
3. The catalyst of claim 1 consisting essentially of platinum, titanium, and tungsten.
4. The catalyst of claim 1 wherein titanium is at a concentration that is no greater than about 80 atomic percent.
5. The catalyst of claim 1 wherein tungsten is at a concentration that is no greater than about 80 atomic percent.
6. The catalyst of claim 1 wherein platinum is at a concentration between about 5 and 60 atomic percent, titanium is at a concentration that is no greater than about 80 atomic percent, and tungsten is at a concentration that is between about 10 and about 80 atomic percent.
7. The catalyst of claim 1 wherein platinum is at a concentration that is between about 10 and about 50 atomic percent, titanium is at a concentration that is between about 1 and about 55 atomic percent, and tungsten is at a concentration that is between about 20 and about 60 atomic percent.
8. The catalyst of claim 1 wherein platinum is at a concentration that is between about 20 and about 45 atomic percent, titanium is at a concentration that is



between about 5 and about 40 atomic percent, and tungsten is at a concentration that is between about 30 and about 55 atomic percent.

9. The catalyst of claim 1 wherein platinum is at a concentration that is between about 30 and about 50 atomic percent, titanium is at a concentration that is no greater than about 20 atomic percent, and tungsten is at a concentration that is between about 40 and about 60 atomic percent.

10. The catalyst of claim 1 wherein platinum is at a concentration that is between about 35 and about 45 atomic percent, titanium is at a concentration that is between about 5 and about 15 atomic percent, and tungsten is at a concentration that is between about 45 and about 55 atomic percent.

11. The catalyst of claim 1 wherein platinum is at a concentration that is between about 20 and about 40 atomic percent, titanium is at a concentration that is between about 25 and about 45 atomic percent, and tungsten is at a concentration that is between about 30 and about 50 atomic percent.

12. The catalyst of claim 1 wherein platinum is at a concentration that is between about 25 and about 35 atomic percent, titanium is at a concentration that is between about 30 and about 40 atomic percent, and tungsten is at a concentration that is between about 35 and about 45 atomic percent.

13. A catalyst for use in oxidation or reduction reactions, the catalyst comprising platinum, titanium at a concentration of at least 20 atomic percent, and tungsten.

14. A catalyst for use in oxidation or reduction reactions, the catalyst comprising platinum, titanium, and tungsten, wherein the concentration of tungsten is at least 25 atomic percent.

15. The catalyst as in any one of claims 1-14 wherein the catalyst is an alloy comprising platinum, titanium, and tungsten.
16. A supported electrocatalyst powder for use in electrochemical reactor devices, the supported electrocatalyst powder comprising the catalyst as in any one of claims 1-15 and electrically conductive support particles upon which the catalyst is dispersed.
17. The supported electrocatalyst powder of claim 16 wherein the electrically conductive support particles are selected from the group consisting of inorganic supports and organic supports.
18. The supported electrocatalyst powder of claim 17 wherein the electrically conductive support particles are selected from the group consisting of carbon supports and electrically conductive polymer supports.
19. A fuel cell electrode, the fuel cell electrode comprising electrocatalyst particles and an electrode substrate upon which the electrocatalyst particles are deposited, the electrocatalyst particles comprising the catalyst as in any one of claims 1-15.
20. The fuel cell electrode of claim 19 wherein the electrocatalyst particles comprise electrically conductive support particles upon which the catalyst is dispersed.
21. The fuel cell electrode of claim 20 wherein the electrically conductive support particles are selected from the group consisting of carbon supports and electrically conductive polymer supports.
22. A fuel cell comprising an anode, a cathode, a proton exchange membrane between the anode and the cathode, and the catalyst as in any one of claims 1-15 for

the catalytic oxidation of a hydrogen-containing fuel or the catalytic reduction of oxygen.

23. The fuel cell of claim 22 wherein the fuel consists essentially of hydrogen.

24. The fuel cell of claim 22 wherein the fuel is a hydrocarbon-based fuel.

25. The fuel cell of claim 22 wherein the fuel comprises methanol.

26. The fuel cell of claim 22 wherein the catalyst is on the surface of the proton exchange membrane and in contact with the anode.

27. The fuel cell of claim 22 wherein the catalyst is on the surface of the anode and in contact with the proton exchange membrane.

28. The fuel cell of claim 22 wherein the catalyst is on the surface of the proton exchange membrane and in contact with the cathode.

29. The fuel cell of claim 22 wherein the catalyst is on the surface of the cathode and in contact with the proton exchange membrane.

30. A method for the electrochemical conversion of a hydrogen-containing fuel and oxygen to reaction products and electricity in a fuel cell comprising an anode, a cathode, a proton exchange membrane therebetween, the catalyst as in any one of claims 1-15, and an electrically conductive external circuit connecting the anode and cathode, the method comprising contacting the hydrogen-containing fuel or the oxygen and the catalyst to catalytically oxidize the hydrogen-containing fuel or catalytically reduce the oxygen.

31. The method of claim 30 wherein the hydrogen-containing fuel consists essentially of hydrogen.

32. The method of claim 30 wherein the hydrogen-containing fuel is a hydrocarbon-based fuel selected from the group consisting of saturated hydrocarbons, garbage off-gas, oxygenated hydrocarbons, fossil fuels, and mixtures thereof.

33. The method of claim 30 wherein the hydrogen-containing fuel is methanol.

34. An unsupported catalyst layer on a surface of an electrolyte membrane or an electrode, said unsupported catalyst layer comprising platinum at a concentration that is less than 60 atomic percent, titanium, and tungsten.

**FUEL CELL ELECTROCATALYST OF Pt-Ti-W****ABSTRACT OF THE DISCLOSURE**

An improved metal alloy composition for a fuel cell electrocatalyst, the metal alloy contains platinum at a concentration that is no greater than 60 atomic percent, titanium, and tungsten.

5

FIG. 1

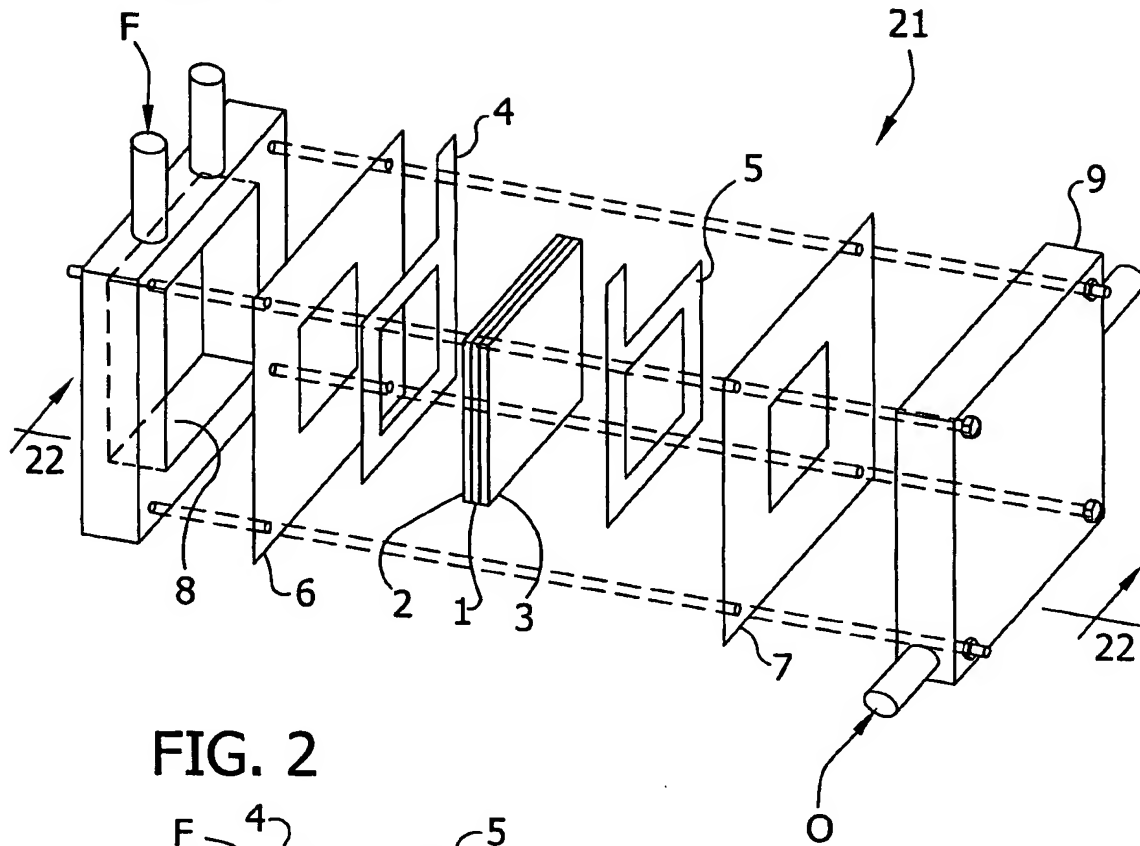


FIG. 2

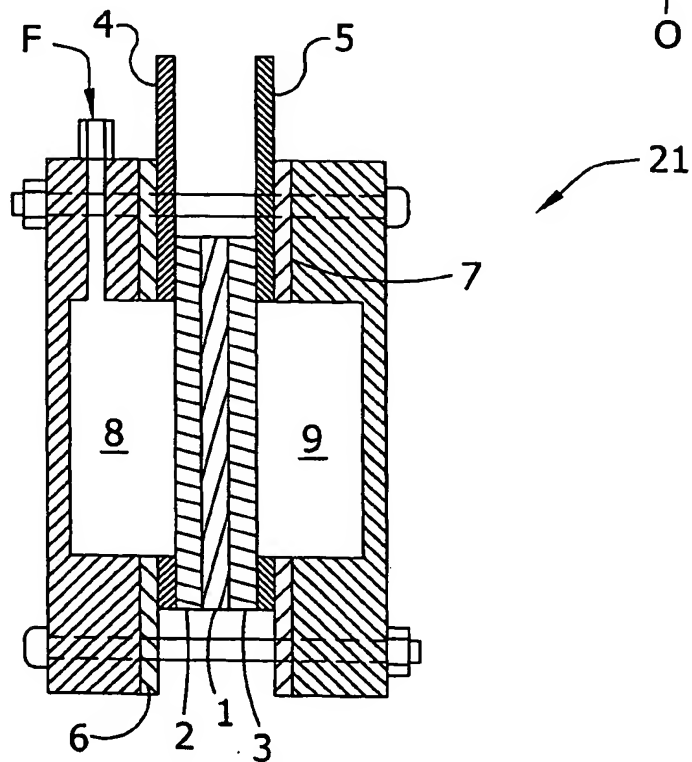
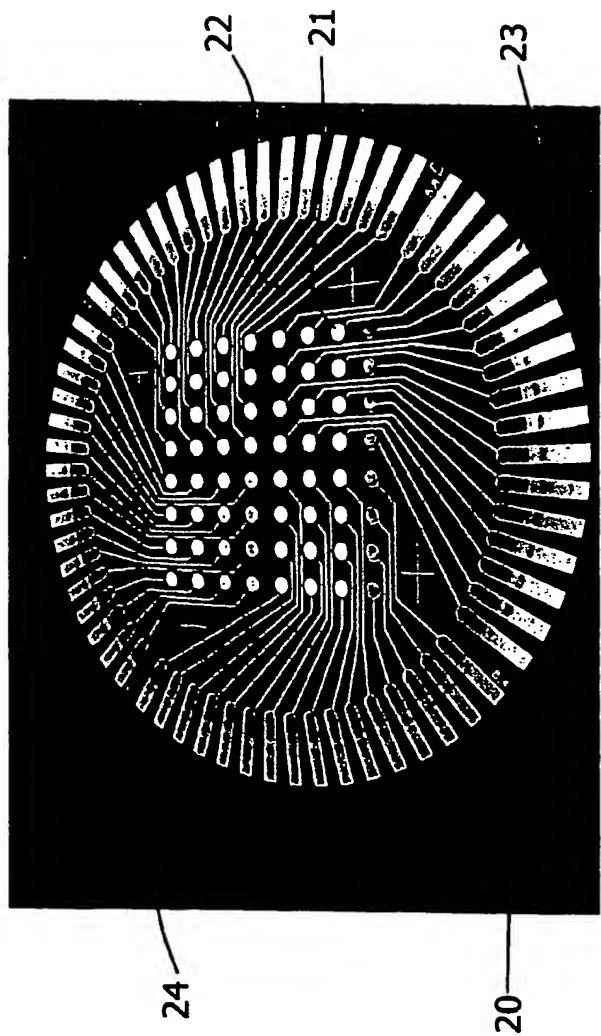


FIG. 3



**APPLICATION DATA SHEET****Application Information**

Application Type::	Provisional
Subject Matter::	Utility
Title::	FUEL CELL ELECTROCATALYST OF Pt-Ti-W
Attorney Docket Number::	SMX 2020 (Symyx Ref. 2002-105) (H103-1731-US01)
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Small Entity?::	No
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